A FURTHER INVESTIGATION OF THE CRYSTAL STRUCTURE OF SODIUM HYPONITRITE

by

GLEN PATRICK REESE

B. S., Montana State College, 1963

A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Physics

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1967

Approved by:

R. D. Dragsdorf
Major Professor

TABLE OF CONTENTS

INTRODUCTION

Previous investigations of the crystal structure of sodium hyponitrite (Chang, 1963) have indicated a trans structure in the $N_2O_2^{-}$ ion as opposed to a cis or isoelectronic configuration. Crystals grown from an aqueous solution were determined to be an octahydrate which decomposed to a pentahydrate on contact with air, and further decomposed to sodium carbonate.

The unit cell parameters of the pentahydrate form were determined through X-ray diffraction studies. Cell axes were chosen such that a space group of the highest possible symmetry consistent with observed reflection conditions could be assigned. The final magnitudes of the monoclinic cell parameters were: $a = 7.22 \pm .03$Å $b = 17.10 \pm .07$Å $c = 6.01 \pm .02$Å $\gamma = 107.5 \pm .4^{\circ}$ with the space group $P2_1/b$. This space group is shown in Plate I. The symmetry elements consist of two-fold screw axes, (ʃ); inversion centers, (0); and a glide plane at $z = \frac{1}{4}$.

Chang also prepared a table of observed structure factor magnitudes, scaled absolutely and corrected for isotropic thermal vibration. This list is presented in Table 1.

The purpose of this research was to proceed from this information to a more complete structure determination of sodium hyponitrite pentahydrate.

X-RAY DIFFRACTION

At this stage of the structure determination the list of observed structure factor magnitudes becomes the focal point of

EXPLANATION OF PLATE I

Fig. 1. The symmetry elements associated with space group $P2_1/b$. Circles represent inversion centers and the curly symbols represent 2-fold screw axes.

Fig. 2. Graphical representation of the equivalent positions of the space group. The numbers show the z coordinates and the comma-symbols represent left-handed molecules.

PLATE I

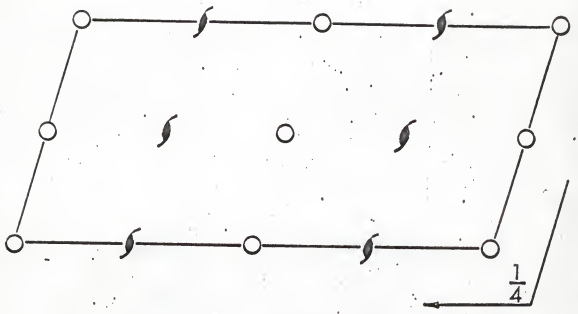


Fig. 1.

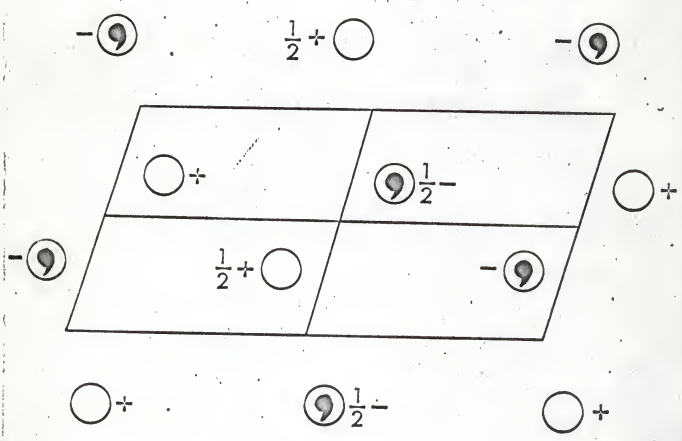


Fig. 2

Table I. The observed structure factors of $Na_2N_2O_2$ as rendered to absolute scale and corrected for thermal vibration.

h	k	l	|F|	h	k	l	|F|	h	k	l	|F|
0	2	0	5.94	6	0	0	0	$\bar{5}$	6	0	8.15
0	4	0	18.92	6	2	0	14.92	$\bar{5}$	8	0	8.50
0	6	0	63.53	6	4	0	28.92	$\bar{5}$	10	0	0
0	8	0	5.61					$\bar{5}$	12	0	0
0	10	0	0	7	0	0	24.42	$\bar{5}$	14	0	23.28
0	12	0	89.68	7	2	0	18.26				
0	14	0	18.40					$\bar{6}$	2	0	0
0	16	0	40.59	$\bar{1}$	4	0	47.32	$\bar{6}$	4	0	9.09
				$\bar{1}$	6	0	59.09	$\bar{6}$	6	0	0
1	0	0	19.34	$\bar{1}$	8	0	17.44	$\bar{6}$	8	0	122.66
1	2	0	15.75	$\bar{1}$	10	0	16.36	$\bar{6}$	10	0	16.76
1	4	0	8.93	$\bar{1}$	12	0	14.12				
1	6	0	14.41	$\bar{1}$	14	0	41.26	$\bar{7}$	2	0	18.97
1	8	0	56.46	$\bar{1}$	16	0	43.81	$\bar{7}$	4	0	26.83
1	10	0	30.70					$\bar{7}$	6	0	0
1	12	0	25.95	$\bar{2}$	2	0	9.49	$\bar{7}$	8	0	15.47
1	14	0	0	$\bar{2}$	4	0	109.51				
1	16	0	24.48	$\bar{2}$	6	0	129.86	0	2	1	18.35
				$\bar{2}$	8	0	23.74	0	3	1	51.39
2	0	0	76.85	$\bar{2}$	10	0	0	0	4	1	22.05
2	2	0	19.70	$\bar{2}$	12	0	0	0	5	1	8.81
2	4	0	20.77	$\bar{2}$	14	0	25.68	0	6	1	23.12
2	6	0	0	$\bar{2}$	16	0	73.83	0	7	1	25.86
2	8	0	51.74	$\bar{2}$	18	0	42.81	0	8	1	45.04
2	10	0	8.63					0	9	1	56.72
2	12	0	21.53	$\bar{3}$	2	0	31.62	0	10	1	19.17
2	14	0	54.33	$\bar{3}$	4	0	4.97	0	11	1	33.86
				$\bar{3}$	6	0	74.64	0	12	1	19.37
3	0	0	29.07	$\bar{3}$	8	0	64.38	0	13	1	33.69
3	2	0	23.60	$\bar{3}$	10	0	0	0	14	1	8.92
3	4	0	20.98	$\bar{3}$	12	0	0	0	15	1	15.14
3	6	0	15.65	$\bar{3}$	14	0	0	0	16	1	8.09
				$\bar{3}$	16	0	8.50				
4	0	0	0					1	0	1	4.72
4	2	0	7.22	$\bar{4}$	2	0	80.31	1	1	1	50.75
4	4	0	35.24	$\bar{4}$	4	0	96.55	1	2	1	12.91
4	6	0	0	$\bar{4}$	6	0	19.92	1	3	1	21.63
4	8	0	81.45	$\bar{4}$	8	0	20.36	1	4	1	52.88
4	10	0	29.28	$\bar{4}$	10	0	0	1	5	1	4.58
				$\bar{4}$	12	0	0	1	6	1	10.25
5	0	0	9.88	$\bar{4}$	14	0	0	1	7	1	24.94
5	2	0	0	$\bar{4}$	16	0	35.27	1	8	1	22.25
5	4	0	0					1	9	1	0
5	6	0	26.24	$\bar{5}$	2	0	38.18	1	10	1	23.72
5	8	0	38.83	$\bar{5}$	4	0	23.12	1	11	1	17.17

Table I (Cont.)

h	k	l	|F|	h	k	l	|F|	h	k	l	|F|
1	12	1	15.59	4	9	1	12.65	$\bar{2}$	1	1	72.43
1	13	1	23.93	4	10	1	12.09	$\bar{2}$	2	1	9.01
1	14	1	0	4	11	1	20.57	$\bar{2}$	3	1	30.27
1	15	1	0	4	12	1	9.08	$\bar{2}$	4	1	28.26
1	16	1	19.54					$\bar{2}$	5	1	4.33
				5	0	1	29.32	$\bar{2}$	6	1	48.52
2	0	1	22.31	5	1	1	0	$\bar{2}$	7	1	54.33
2	1	1	36.33	5	2	1	0	$\bar{2}$	8	1	8.02
2	2	1	98.71	5	3	1	12.80	$\bar{2}$	9	1	50.00
2	3	1	60.63	5	4	1	0	$\bar{2}$	10	1	43.57
2	4	1	20.34	5	5	1	0	$\bar{2}$	11	1	23.10
2	5	1	109.54	5	6	1	21.96	$\bar{2}$	12	1	0
2	6	1	42.22	5	7	1	0	$\bar{2}$	13	1	21.70
2	7	1	0	5	8	1	0	$\bar{2}$	14	1	8.98
2	8	1	22.69	5	9	1	18.98	$\bar{2}$	15	1	0
2	9	1	11.60	5	10	1	8.43	$\bar{2}$	16	1	0
2	10	1	0					$\bar{2}$	17	1	0
2	11	1	0	6	0	1	18.26	$\bar{2}$	18	1	14.24
2	12	1	9.07	6	1	1	24.25				
2	13	1	12.28	6	2	1	11.05	$\bar{3}$	1	1	21.77
2	14	1	27.61	6	3	1	22.53	$\bar{3}$	2	1	32.67
				6	4	1	0	$\bar{3}$	3	1	0
3	0	1	7.21	6	5	1	14.16	$\bar{3}$	4	1	27.24
3	1	1	56.90	6	6	1	13.08	$\bar{3}$	5	1	0
3	2	1	20.38					$\bar{3}$	6	1	13.65
3	3	1	42.77	7	0	1	15.57	$\bar{3}$	7	1	29.11
3	4	1	18.43	7	1	1	0	$\bar{3}$	8	1	24.81
3	5	1	14.91	7	2	1	6.59	$\bar{3}$	9	1	44.83
3	6	1	18.72					$\bar{3}$	10	1	7.53
3	7	1	44.03	$\bar{1}$	1	1	13.06	$\bar{3}$	11	1	33.21
3	8	1	8.78	$\bar{1}$	2	1	9.49	$\bar{3}$	12	1	8.58
3	9	1	12.76	$\bar{1}$	3	1	12.24	$\bar{3}$	13	1	9.02
3	10	1	20.49	$\bar{1}$	4	1	0	$\bar{3}$	14	1	18.23
3	11	1	0	$\bar{1}$	5	1	0	$\bar{3}$	15	1	27.99
3	12	1	0	$\bar{1}$	6	1	15.59	$\bar{3}$	16	1	8.37
3	13	1	7.84	$\bar{1}$	7	1	10.86	$\bar{3}$	17	1	10.57
3	14	1	13.87	$\bar{1}$	8	1	46.48				
				$\bar{1}$	9	1	0	$\bar{4}$	1	1	41.68
4	0	1	13.61	$\bar{1}$	10	1	12.08	$\bar{4}$	2	1	34.35
4	1	1	34.73	$\bar{1}$	11	1	0	$\bar{4}$	3	1	24.09
4	2	1	12.88	$\bar{1}$	12	1	0	$\bar{4}$	4	1	14.03
4	3	1	7.79	$\bar{1}$	13	1	17.79	$\bar{4}$	5	1	18.82
4	4	1	27.04	$\bar{1}$	14	1	17.96	$\bar{4}$	6	1	0
4	5	1	44.62	$\bar{1}$	15	1	8.92	$\bar{4}$	7	1	17.48
4	6	1	15.48	$\bar{1}$	16	1	0	$\bar{4}$	8	1	0
4	7	1	0	$\bar{1}$	17	1	18.14	$\bar{4}$	9	1	5.56
4	8	1	0	$\bar{1}$	18	1	14.65	$\bar{4}$	10	1	37.87

Table I (Cont.)

h	k	l	|F|	h	k	l	|F|	h	k	l	|F|
$\bar{4}$	11	1	30.21	0	6	2	20.11	3	5	2	0
$\bar{4}$	12	1	27.02	0	7	2	4.23	3	6	2	44.93
$\bar{4}$	13	1	59.88	0	8	2	73.23	3	7	2	0
$\bar{4}$	14	1	20.61	0	9	2	60.51	3	8	2	0
$\bar{4}$	15	1	19.31	0	10	2	16.87	3	9	2	9.98
$\bar{4}$	16	1	20.86	0	11	2	37.36	3	10	2	26.04
				0	12	2	9.79	3	11	2	0
$\bar{5}$	1	1	24.92	0	13	2	0	3	12	2	0
$\bar{5}$	2	1	0	0	14	2	0	3	13	2	29.00
$\bar{5}$	3	1	9.95	0	15	2	16.63				
$\bar{5}$	4	1	19.04	0	16	2	40.69	4	0	2	32.13
$\bar{5}$	5	1	0					4	1	2	32.13
$\bar{5}$	6	1	17.54	1	0	2	19.03	4	2	2	0
$\bar{5}$	7	1	28.05	1	1	2	51.50	4	3	2	0
$\bar{5}$	8	1	0	1	2	2	65.99	4	4	2	22.72
$\bar{5}$	9	1	34.50	1	3	2	5.33	4	5	2	19.12
$\bar{5}$	10	1	0	1	4	2	5.01	4	6	2	33.80
$\bar{5}$	11	1	19.16	1	5	2	37.91	4	7	2	69.84
$\bar{5}$	12	1	23.89	1	6	2	0	4	8	2	20.48
$\bar{5}$	13	1	10.80	1	7	2	34.60	4	9	2	17.12
$\bar{5}$	14	1	0	1	8	2	0	4	10	2	0
$\bar{5}$	15	1	15.87	1	9	2	0	4	11	2	7.46
				1	10	2	0				
$\bar{6}$	1	1	31.94	1	11	2	0	5	0	2	9.71
$\bar{6}$	2	1	30.32	1	12	2	21.88	5	1	2	0
$\bar{6}$	3	1	0	1	13	2	34.90	5	2	2	11.98
$\bar{6}$	4	1	0					5	3	2	34.12
$\bar{6}$	5	1	25.83	2	0	2	54.51	5	4	2	27.86
								5	5	2	0
$\bar{6}$	6	1	0	2	1	2	12.76	5	6	2	32.66
$\bar{6}$	7	1	0	2	2	2	14.66	5	7	2	11.06
$\bar{6}$	8	1	0	2	3	2	8.00	5	8	2	0
$\bar{6}$	9	1	0	2	4	2	64.76	5	9	2	6.43
$\bar{6}$	10	1	28.23	2	5	2	0				
$\bar{6}$	11	1	24.51	2	6	2	0	6	0	2	43.11
$\bar{6}$	12	1	0	2	7	2	8.22	6	1	2	19.08
$\bar{6}$	13	1	18.37	2	8	2	39.91	6	2	2	9.43
				2	9	2	16.25	6	3	2	0
$\bar{7}$	1	1	12.71	2	10	2	39.84	6	4	2	0
$\bar{7}$	2	1	13.11	2	11	2	37.04	6	5	2	0
$\bar{7}$	3	1	0	2	12	2	0	6	6	2	17.16
$\bar{7}$	4	1	13.42	2	13	2	9.16				
								7	1	2	15.16
0	1	2	31.31	3	0	2	10.89				
0	2	2	14.14	3	1	2	53.98	$\bar{1}$	1	2	12.27
0	3	2	70.55	3	2	2	18.23	$\bar{1}$	2	2	36.33
0	4	2	56.15	3	3	2	14.60	$\bar{1}$	3	2	28.09
0	5	2	4.82	3	4	2	15.57	$\bar{1}$	4	2	5.06

Table I (Concl.)

h	k	l	|F|	h	k	l	|F|	h	k	l	|F|
$\bar{1}$	5	2	25.50	$\bar{4}$	1	2	38.54	$\bar{7}$	1	2	12.35
$\bar{1}$	6	2	5.38	$\bar{4}$	2	2	29.00	$\bar{7}$	2	2	0
$\bar{1}$	7	2	19.67	$\bar{4}$	3	2	21.87	$\bar{7}$	3	2	24.89
$\bar{1}$	8	2	40.35	$\bar{4}$	4	2	16.47	$\bar{7}$	4	2	0
$\bar{1}$	9	2	0	$\bar{4}$	5	2	49.66	$\bar{7}$	5	2	11.87
$\bar{1}$	10	2	35.34	$\bar{4}$	6	2	34.55	$\bar{7}$	6	2	23.36
$\bar{1}$	11	2	41.30	$\bar{4}$	7	2	0	$\bar{7}$	7	2	15.16
$\bar{1}$	12	2	31.06	$\bar{4}$	8	2	47.04	$\bar{7}$	8	2	0
$\bar{1}$	13	2	21.78	$\bar{4}$	9	2	18.98	$\bar{7}$	9	2	0
$\bar{1}$	14	2	25.80	$\bar{4}$	10	2	0	$\bar{7}$	10	2	33.86
$\bar{1}$	15	2	9.39	$\bar{4}$	11	2	0				
$\bar{1}$	16	2	0	$\bar{4}$	12	2	27.48				
$\bar{1}$	17	2	14.04	$\bar{4}$	13	2	0				
				$\bar{4}$	14	2	9.38				
$\bar{2}$	1	2	15.43	$\bar{4}$	15	2	27.02				
$\bar{2}$	2	2	36.99	$\bar{4}$	16	2	9.07				
$\bar{2}$	3	2	44.73								
$\bar{2}$	4	2	4.99	$\bar{5}$	1	2	9.60				
$\bar{2}$	5	2	5.38	$\bar{5}$	2	2	0				
$\bar{2}$	6	2	9.07	$\bar{5}$	3	2	26.19				
$\bar{2}$	7	2	40.84	$\bar{5}$	4	2	0				
$\bar{2}$	8	2	51.60	$\bar{5}$	5	2	27.82				
$\bar{2}$	9	2	29.35	$\bar{5}$	6	2	0				
$\bar{2}$	10	2	0	$\bar{5}$	7	2	9.66				
$\bar{2}$	11	2	0	$\bar{5}$	8	2	9.84				
$\bar{2}$	12	2	21.96	$\bar{5}$	9	2	29.84				
$\bar{2}$	13	2	11.91	$\bar{5}$	10	2	33.66				
$\bar{2}$	14	2	21.64	$\bar{5}$	11	2	0				
$\bar{2}$	15	2	76.67	$\bar{5}$	12	2	0				
$\bar{2}$	16	2	48.48	$\bar{5}$	13	2	0				
				$\bar{5}$	14	2	0				
$\bar{3}$	1	2	6.13	$\bar{5}$	15	2	17.98				
$\bar{3}$	2	2	22.36								
$\bar{3}$	3	2	37.94	$\bar{6}$	1	2	0				
$\bar{3}$	4	2	0	$\bar{6}$	2	2	0				
$\bar{3}$	5	2	28.81	$\bar{6}$	3	2	0				
$\bar{3}$	6	2	13.58	$\bar{6}$	4	2	21.97				
$\bar{3}$	7	2	14.44	$\bar{6}$	5	2	13.90				
$\bar{3}$	8	2	28.62	$\bar{6}$	6	2	0				
$\bar{3}$	9	2	18.38	$\bar{6}$	7	2	15.00				
$\bar{3}$	10	2	0	$\bar{6}$	8	2	31.74				
$\bar{3}$	11	2	33.04	$\bar{6}$	9	2	24.92				
$\bar{3}$	12	2	21.41	$\bar{6}$	10	2	0				
$\bar{3}$	13	2	0	$\bar{6}$	11	2	33.92				
$\bar{3}$	14	2	37.22	$\bar{6}$	12	2	32.58				
$\bar{3}$	15	2	9.24								
$\bar{3}$	16	2	0								
$\bar{3}$	17	2	6.81								

interest. A structure factor represents the amplitude and phase of a wave scattered from a particular set of crystal planes. Each is a function of all the positions of the atoms within a unit cell. The nature of this relationship will be shown here.

Atomic Scattering Factor

An electron struck by an unpolarized beam of x-rays oscillates and re-emits radiation in all directions. This scattered radiation has the same wavelength as the incident radiation and the scattered intensity, I, exhibits an angular dependence as shown in the J. J. Thomson scattering equation:

$$I = I_o \frac{e^4}{r^2 m^2 c^4} \left(\frac{1 + \cos^2 2\theta}{2}\right) \qquad (1)$$

e = electronic charge
r = distance from oscillating electron
m = electronic mass
c = velocity of light
2θ = scattering angle

Given an aggregate of electrons, as in an atom, each will re-emit radiation according to this formula, but now the fact that the electrons are situated at different points in space introduces phase differences between the scattered waves. Clearly, at a scattering angle of 0°, the phase differences of all scattered waves will be zero as each wave travels the same distance before and after scattering. At scattering angles different from zero, however, path length differences produce partial interference with a resulting loss in net amplitude.

The quantity which describes the efficiency of a given atom type to scatter in a given direction is called the "atomic scattering factor" and is defined as

$$f = \frac{\text{amplitude of scattering from the atom}}{\text{amplitude of scattering from one electron}} \qquad (2)$$

In the forward direction, then, f will equal Z, the number of electrons in the atom, since all electrons scatter in phase. As the scattering angle increases, f decreases due to interference effects. Quantitative considerations of the scattering from the orbital electrons of the various elements yields theoretical expressions for the atomic scattering factors (McLachlan, 1957). Curves and tables of these have been determined for all atomic numbers in all scattering angles. Shown in Plate II are three such curves. These are the scattering factor values used in this structure problem, where singly ionized sodium, Na^+, and singly ionized oxygen, O^-, were assumed.

The selection of these ions was based on trial-and-error computations; other degrees of ionization were tried, and this combination was the one which produced the best fit of the data.

Structure Factor

Given an arrangement of atoms, each will scatter according to its atomic scattering factor. However, the spatial differences in atomic positions now yield further interference conditions. If all atoms are situated randomly, all scattered waves add with random phases, giving a diffuse scattering effect.

EXPLANATION OF PLATE II

The atomic scattering factor curves as functions of $\sin\theta/\lambda$ for Na^+, N, and O^-.

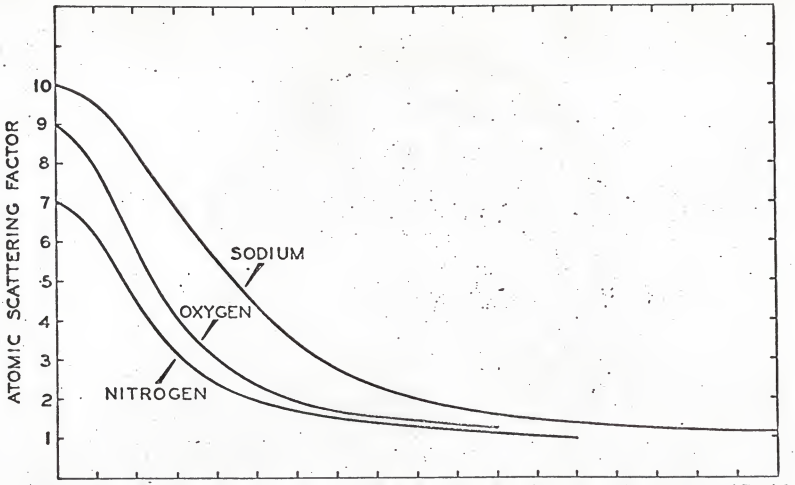

ATOMIC SCATTERING FACTOR
10
9
8
7
6
5
4
3
2
1
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
SODIUM
OXYGEN
NITROGEN
SIN θ/λ (A⁻¹)

PLATE II

If the atomic arrangement is periodic, however, the finite number of interference conditions in a given unit cell will be repeated in the next cell, reinforcing the maxima and minima. With a large number of such cells the diffraction pattern approaches a representation in delta functions. A diffraction spot from a particular orientation of a crystal is labeled with the Miller indices of the set of planes which satisfy the Bragg condition for that orientation. The quantity which describes the relative amplitude and phase of the radiation producing the diffraction spot is termed the "structure factor" for that particular orientation. The structure factor is found by summing the contributions from all atoms in a unit cell. This, in complex notation, becomes

$$F(hk\ell) = \sum_n f_n \exp(2\pi i \phi_n) \tag{3}$$

where the exponential factor accounts for the phase of a wave from a particular atom, in reference to the unit cell origin. The phase factor of an atom located at fractional coordinates (x,y,z) may be shown to be (Cullity, 1959)

$$\phi = hx+ky+\ell z \tag{4}$$

It is seen, then, that F is defined as a ratio of amplitudes

$$F = \frac{\text{amplitude of scattering from unit cell}}{\text{amplitude of scattering from electron}} \tag{5}$$

and will be independent of the shape and size of the unit cell.

Measurement of Diffraction Lines

There are five other factors, besides the scattering, that affect the intensity of diffraction lines. These are

(1) polarization
(2) multiplicity
(3) Lorentz effect
(4) absorption
(5) temperature

In an actual measurement of diffracted intensities the corrections for these may be readily applied (Cullity, 1959), with the possible exception of the last factor. The first four are obtainable from parameters of the experiment, e.g., diffraction angle, crystal morphology, and structure. The temperature factor is a measure of atomic thermal vibration and is often treated as an unknown, to be determined along with the atom positions. Since the temperature effect is generally quite small the structure determination proceeds without this correction until the refinement phase is reached. At this point the temperature factor is introduced in the form of a perturbation on the structure factors.

X-ray diffraction patterns are generally recorded on photographic film or by radiation counters which count in proportion to the number of quanta received per unit time. These methods yield the intensity of the diffraction line. However, as is well known, the intensity will determine only the square of the amplitude of the diffracted wave, since

$$I \sim F^{*}F . \qquad (6)$$

Data reduction then yields a table of structure factor magnitudes. The phases of the diffracted waves are undetermined by these methods; the data are incomplete. This is the fundamental problem of crystallography and referred to as the phase problem.

The Phase Problem

The phase of a wave diffracted from a set of planes is measured relative to a wave scattered from parallel planes which pass through the origins of the cells. A knowledge of this phase determines the absolute placement of the given set of planes within the unit cells. This concept is basic to the elegant 3-dimensional Fourier series representation of the structure. To illustrate this, consider a one-dimensional crystal having structure factors

$$F(h) = \sum_j f_j \exp(2\pi i h x_j) \ . \tag{7}$$

Instead of assuming discrete atoms, assume a continuous distribution of electrons along a. The series representing scattered waves is now replaced by an integration from 0 to a.

$$F(h) = \int_0^a \rho(x) \exp(2\pi i h x) dx \tag{8}$$

This is recognizable as a Fourier coefficient of the series

$$\rho(x) = \frac{1}{a} \sum_{h=-\infty}^{\infty} F(h) \exp(-2\pi i h x) . \tag{9}$$

In the three dimensional analysis this becomes

$$\rho(x) = \frac{1}{V} \sum_{n} \sum_{k} \sum F(hk\ell)\exp(-2\pi i(hx+ky+\ell z)). \qquad (10)$$

In this manner a knowledge of the structure factors allows an electron density map to be synthesized. The regions of maximum electron density are chosen as the atom locations.

However, the determination of shape and size of the unit cell does not fix the location of the unit cell origin with respect to an atom or set of planes. It may well be that a certain choice of origin will be such as to take advantage of relations between atom positions, giving an analytical expression to the position of one or more in terms of another. These relations are the symmetry operations of a space group and can reduce the number of unknown positions by their simplification of the structure factor equations. These also yield conditions on certain sets of structure factors; indeed, it is the recognition of a particular set of these conditions that yields the space group determination.

The abject futility of attempting to guess the unknown phases may be illustrated by a realistic example. Given a typical structure, some four hundred independent reflections may be present. If space group symmetry is such that phases are limited to $\pm 180^{\circ}$, (F is real, but undetermined in sign) this yields 2^{400} variables to be simultaneously chosen. A high speed computer guessing and checking at the rate of one set per second would require roughly 2^{369} centuries to arrive at the correct set. More devious methods must be applied and some of these will be discussed later as they were applied in this structure problem.

EXPERIMENTAL PROCEDURE

Reduction of Equations

The $P2_1/b$ space group has equivalent atoms at coordinates (xyz), $(\bar{x}\bar{y}\bar{z})$, $(\bar{x},\frac{1}{2}-y,\frac{1}{2}+z)$, $(x,\frac{1}{2}+y,\frac{1}{2}-z)$. This is immediately seen to be a centrosymmetric structure. Substitution of these relations into the structure factor equations yields the following conditions:

$$h+k+\ell = n \quad : \quad \begin{cases} F(hk\ell) \text{ is real} \\ F(hk\ell) = F(\bar{h}\bar{k}\bar{\ell}) \end{cases}$$

$$k+\ell = 2n \quad : \quad F(hk\ell) = F(hk\bar{\ell}); \; F(\bar{h}k\ell) = F(h\bar{k}\ell)$$

$$k+\ell = 2n+1 \quad : \quad F(hk\ell) = -F(hk\bar{\ell}) \quad F(\bar{h}k\ell); \; F(\bar{h}k\ell) = -F(h\bar{k}\ell)$$

with the requirements on nonzero reflections that

$$\ell = 0 \quad : \quad k = 2n$$

$$h = k = 0 \quad : \quad \ell = 2n$$

The equations of interest have the particular form

$$F(hk\ell) = 2\sum_j f_j \cos 2\pi(hx_j+ky_j+\ell z_j) \tag{11}$$

where the sum does not include centrosymmetrical partners, and

$$\rho(x,y,z) = \sum_h \sum_k \sum_\ell \pm \left|F(hk\ell)\right| \cos 2\pi(hx+ky+\ell z) \tag{12}$$

Determination of Cell Density

Chemical Method. In order to properly use the structure factor equations, it is vital to know the number and type of molecules per unit cell. The number of molecules/unit cell, n, is usually determined by the formula

$$n = \frac{(N \text{ molecules/mole})\ (\rho \text{gm/cm}^3)\ (V \text{ cm}^3\text{/unit cell}}{(A \text{ gm/mole})}.$$

This requires accurate determination of ρ and V, and knowledge of the chemical formula, so that A may be found. Density measurements of the compound, using the Karle-Fischer reagent technique (Stucky, Lambert, and Dragsdorf, 1966), did not confirm the original hypothesis of 5 waters/molecule, but indicated that the so-called "pentahydrate" contained $3\frac{1}{2}$ waters/molecule, with 4 molecules/unit cell.

While the 4 molecules/cell determination is fairly certain, the reproducibility of the measurements was not such as to pin down the number of waters per molecule. Although the hypothesis of $3\frac{1}{2}$ seemed most probable, error limits allowed all choices from two to five. The methods of chemistry seemed inadequate to determine these elusive parameters more accurately, and such methods were abandoned at this point.

Statistical Method. Hauptmann and Karle (1953) attacked the phase problem by a direct statistical approach. In their work they used a "normalized" structure factor defined by

$$E^2(hk\ell) = \frac{|F(hk\ell)|^2}{\xi \sum_{j=1}^{k} f_j^2(hk\ell)} \qquad (13)$$

where ϵ takes on the value of 1 or 2 in this problem, depending upon the reflection in consideration. Among other properties, to be treated later, was the existence of average values of functions of the $|E(hk\ell)|$ and probability distributions of this quantity. For a random structure the theoretical statistical averages are

Centrosymmetric	Non-Centrosymmetric
$\langle\|E\|\rangle = .798$	.886
$\langle\|E^2-1\|\rangle = .968$	.736
$\langle E^2\rangle = 1.000$	1.000

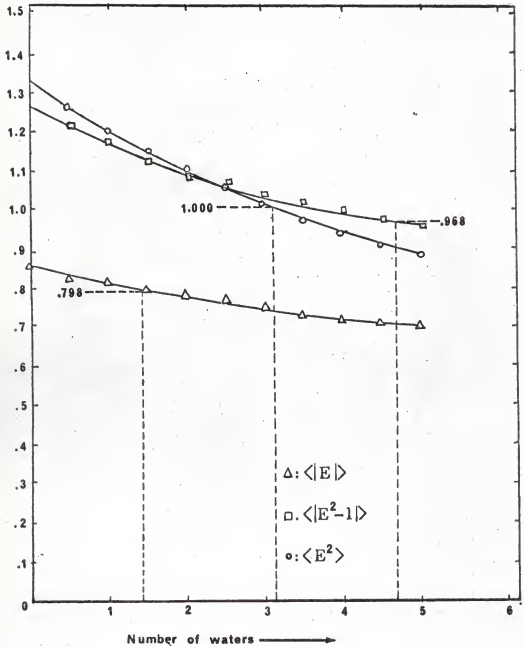
Recognizing that the E values are dependent upon the number of atoms per unit cell, it was decided to calculate these averages and distributions for assumed waters of hydration from none through five in half-integral steps. The calculation was done on the IBM 1410 computer. The results of this calculation are graphically displayed on Plate III and were seen to be inconclusive, insofar as to determine the exact number of waters. However, the calculation does indicate, quite definitely, that the structure is indeed centrosymmetric.

On the basis of such difficulties, it was hypothesized that the waters of hydration are bonded loosely and do not occupy well-defined positions in the structure. In the extreme case of complete randomness of the water positions, the effect on the diffraction pattern would be only to increase background intensity; the space group for the remaining atoms would be unaffected. This hypothesis is strengthened by the apparent

EXPLANATION OF PLATE III

$\langle|E|\rangle$, $\langle|E^2-1|\rangle$, and $\langle E^2\rangle$ related to the number of waters of hydration in the hyponitrite crystal. Also indicated are the theoretically expected values for a centrosymmetric crystal.

PLATE III


1.5
1.4
1.3
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
1.000
.968
.798
Δ: ⟨|E|⟩
□. ⟨|E²−1|⟩
o: ⟨E²⟩
1
2
3
4
5
6
Number of waters

mobility of the waters in their ability to leave the lattice completely, i.e., the instability of the "pentahydrate."

The problems imposed by lack of knowledge of cell density are by no means insurmountable. The methods of structure determination adapt to treatment of this added unknown and such work began at this point.

Direct Solution of the Structure

Ignoring the waters for the time being, it was seen that six atom positions were to be determined. The other 18 positions would be determined by the symmetry relations. There were eight reflections in the 0k0 class and seven in the h00 class. The structure factor equations reduce to one-dimensional equations under such conditions. An attempt to solve these two nonlinear systems was made to determine the x and y coordinates of the six unknown atoms. The systems were overdetermined but the indeterminacy of signs on the F (hkℓ) was present. It was hoped that only one combination of signs would yield a consistent system. Efforts to invert the system to obtain explicit equations for the (x,y) coordinates were fruitless, so a brute-force technique was employed. The computer was programmed to select values systematically for the variables, substitute into the equations, and determine the goodness of fit. The results were inconclusive as many combinations of variables produced the same degree of success.

Statistical Analysis

A direct approach to the phase problem has been described by Karle and Hauptmann (1953). This process involves the normalized structure factors, $E^2(hk\ell)$, which have been defined earlier by Equation (13).

The basis of this procedure rests on the relation

$$sE(h+h',\ k+k',\ \ell+\ell') = sE(hk\ell)\cdot sE(h'k'\ell').$$

s = "sign of"

The probability that a sign determined by this relation is positive is given by

$$P_+(E(hk\ell)) = \tfrac{1}{2}+\tfrac{1}{2}\tanh\left(E(hk\ell)\right)\frac{\sum_{h'}\sum_{k'}\sum_{\ell'} E(h-h',\ k-k',\ \ell-\ell')\cdot E(h'k'\ell')}{\sqrt{N}} \qquad (14)$$

N = number of interactions

The larger the magnitudes of the interacting factors, the greater is the probability of success. Three large and linearly independent structure factors were selected to initiate the process and chosen to be positive. (Three such signs may be chosen arbitrarily; other signs will depend on this choice.) As the signs of other structure factors were determined with high reliability, they were included in the interaction equations. The possible number of determinations was limited by a shortage of z-data; the ℓ Miller index (See Table 1) included values only to two. Consequently, this approach did not

determine enough signs to be of significant value and was abandoned.

Patterson Function

One of the most widely used devices in crystallography is the "Patterson function," introduced by A. L. Patterson in 1935. In three dimensions it has the form

$$P(x,y,z) = \frac{1}{V}\iiint \rho(u+x,v+y,w+z)\,\rho(u,v,w)\,du\,dv\,dw \qquad (15)$$

V = cell volume

ρ = electron density

The integration is taken over one unit cell. This function is seen to be a self-convolution of the electron density function. Patterson showed that the function may also be expressed in the form

$$P(x,y,z) = \sum_h \sum_k \sum_\ell |F(hk\ell)|^2 \cos 2\pi(hx+ky+\ell z) \qquad (16)$$

which is seen to be centrosymmetric. The Patterson function may be computed with no knowledge of the phase values of the $F(hk\ell)$. If one of the coordinates is assigned a constant value, a "section" of the function in the plane of the constant coordinate is obtained. If one of the indices is assigned a zero value, the summation includes contributions from planes parallel to the conjugate coordinate axis, and a "projection" of the function onto the plane perpendicular to that axis is obtained. Sections and projections are the most usable forms of the

Patterson function.

More insight into the nature of the function may be gained by noting the following. In general

$$F(hk\ell) = \sum_j f_j \exp(2\pi i(hx_j+ky_j+\ell z_j)) \tag{17}$$

$$F^2(hk\ell) = \sum_i \sum_j f_i f_j \exp(2\pi i\{h(x_i-x_j)+k(y_i-y_j)+\ell(z_i-z_j)\}) \tag{18}$$

Just as $F(hk\ell)$ represents the Fourier transform of a structure having atoms of scattering factors f_j located at (x_j,y_j,z_j), so does $F(hk\ell)^2$ represent a structure having "atoms" of scattering factor $f_i f_j$ located at $(\underline{r}_i-\underline{r}_j)$. The density peaks of the Patterson function are not located at the positions of the original atoms but at the vectorial differences of the atom positions. The Patterson function of a structure containing n distinct atoms will contain n(n-1) distinct peaks; the original structure is repeated n times in the Patterson map. The most expedient method in which to display a Patterson function is in the form of a topographical map. This allows the visualization of possible molecular configurations as well as quantitative information, when so desired. A high-speed computer mapping program was prepared by R. L. Hollis and used to make the Patterson function maps for this crystal. Plate IV shows the projection along the z axis. The unit cell has been divided into a network of grids and the functional value computed for the center of each grid. Each character on the map represents the functional density interval into which the value of the function falls at

EXPLANATION OF PLATE IV

The z-projection of the Patterson function for sodium hyponitrite.

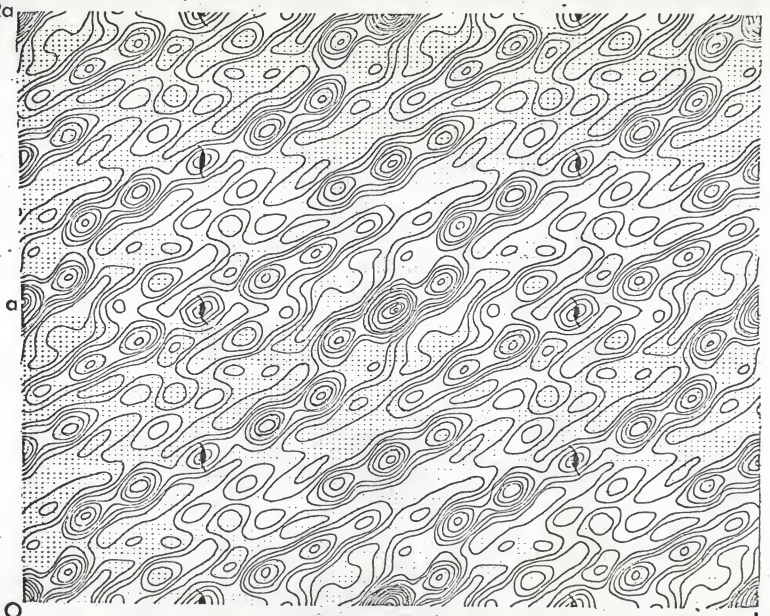


PLATE IV

* Due to a typing error, page no. 27 was omitted.
This page is inserted to avoid confusion.

that point. Contour lines have been drawn to indicate isobars of functional density.

Simply stated, one attempts to select a set of peaks from the Patterson map that, when self-convoluted, will reproduce the entire map. The absolute positioning of the set of points within the unit cell is not determined by this but may be aided by symmetry and chemical considerations. The exploitation of symmetry properties of this crystal is outlined below.

Choice of Trial Structure

As previously noted, there exist positions of equivalence in the $P2_1/b$ space group. That is, for a given atom at position $\underline{r}$, there will be identical atoms at positions $\underline{r}+\underline{p}_i(\underline{r})$, where i = 1,2,3. With this in mind, the Patterson function is written down and investigated.

$$P(\underline{x}) = \iiint \rho(\underline{r})\,\rho(\underline{r}+\underline{x})\,d\underline{r} \qquad (19)$$

It is seen from the equation that if $\underline{x}$ is one of the vectors $\underline{p}_i(\underline{r})$, the Patterson function will represent the folding of an atom at $\underline{r}$ with its space group neighbor of identical kind. If such peaks are recognized in the Patterson function, the equations for the $\underline{p}_i(\underline{r})$ may be inverted to obtain possible locations for atoms. The height of such peaks will determine what kinds of atoms they represent. Explicit investigation of the symmetries of this crystal may lend more clarity to this proposition.

The equivalent positions are given by

1) (x,y,z)

2) $(\bar{x},\bar{y},\bar{z})$

3) $(\bar{x},\frac{1}{2}-y,\frac{1}{2}+z)$

4) $(x,\frac{1}{2}+y,\frac{1}{2}-z)$.

The explicit Patterson function is given by

$$P(u,v,w) = \frac{1}{V}\iiint \rho(x,y,z)\,\rho(x+u,y+v,z+w)\,dxdydz \qquad (15)$$

Consider a folding of atom 1) with atom 3). This will take place when the arguments of the integral are such that

$$\begin{aligned} x+u &= \bar{x} \\ y+v &= \tfrac{1}{2}-y \\ z+w &= \tfrac{1}{2}+z. \end{aligned} \qquad (20)$$

Solving these equations yields the coordinates of the Patterson map at which this peak appears.

$$\begin{aligned} u &= -2x \\ v &= \tfrac{1}{2}-2y \\ w &= \tfrac{1}{2} \end{aligned} \qquad (21)$$

Similarly, the folding of atoms 2) and 4) appears at Patterson coordinates

$$\begin{aligned} u &= 2x \\ v &= 2y+\tfrac{1}{2} \\ w &= \tfrac{1}{2}. \end{aligned} \qquad (22)$$

Other combinations are not as interesting. The thing to

recognize is that folding of all equivalent atoms appears at the Patterson section $w = \frac{1}{2}$. (This is not to say that folding of unlike atoms will not also be present.) If a peak in the Patterson section at $w = \frac{1}{2}$ is interpreted as an equivalent atom folding, it is an easy matter to invert the Patterson coordinates of the peak to obtain the unit cell coordinates. From the above equations,

$$\begin{aligned} x &= u/2 \\ y &= (v+\tfrac{1}{2})/2 \end{aligned} \tag{23}$$

$$\begin{aligned} x &= u/2 \\ y &= (v-\tfrac{1}{2})/2 \end{aligned} \tag{24}$$

are the possibilities for atom positions. Note that this procedure says nothing about the z position of the atoms. This is not prohibitive, however, for the structure may be treated in two dimensions at a time.

A tabulation of all peaks in the Patterson section at $w = \frac{1}{2}$, then, will produce all possibilities of unique atom locations in the unit cell. This section is shown in Plate V, and from this was eventually chosen the trial structure which produced the best fit of the data. Such choices are in no way random, for molecular bond lengths must agree with previous knowledge and, in this case, the molecular shape had to be consistent with previous indications of a trans configuration.

Once a trial structure has been selected the problem becomes one of testing its validity and making refinements if it

EXPLANATION OF PLATE V

The Patterson section of sodium hyponitrite at $z = \frac{1}{2}$.

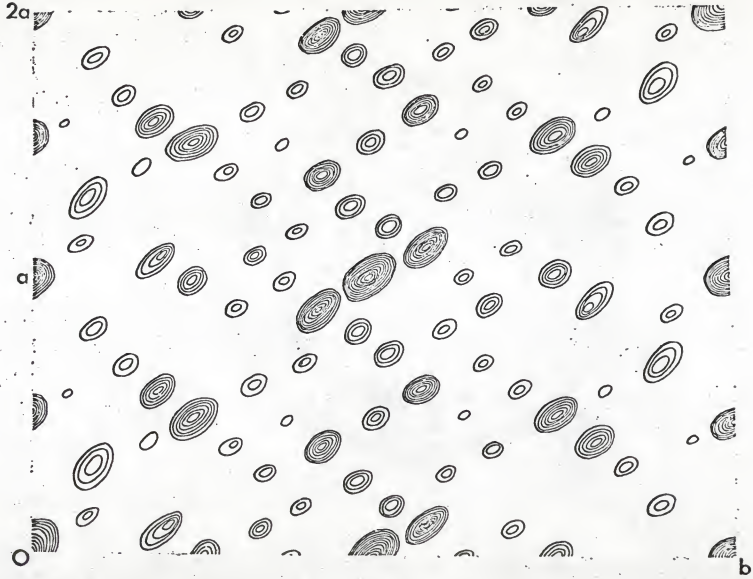


PLATE V

appears to hold promise. Such techniques are outlined below.

The Reliability, R, Factor

The substitution of trial coordinates and the atomic scattering factors into the crystalline structure factor equation for each observed reflection will yield the structure factors of the proposed structure. The magnitudes of these structure factors are compared with those observed. A concise way of expressing the agreement is desirable and this is accomplished by use of the "R factor." The R factor is defined as

$$R = \frac{\sum_{h,k,\ell} \left| |F_o| - |F_c| \right|}{\sum_{h,k,\ell} |F_o|} \qquad (25)$$

F_o = observed $F(hk\ell)$

F_c = calculated $F(hk\ell)$

Experience has shown that a trial structure yielding an R value of .50 or less is worthy of an attempt at refinement. Furthermore, a refined structure having an R value of .05 or less may be considered to be the correct structure. That is, no wrong structure will yield an R value this low (Buerger, 1962).

The trial structure eventually refined had an initial R value of .49 for the z projection. Recall that this projection is acquired by using the hk0 structure factors. Several methods of refinement were used.

Electron Density Map

If the trial structure yields a reasonable R value, it is only because the observed and calculated magnitudes of the $F(hk\ell)$ are in good agreement. This is particularly true of the larger $F(hk\ell)$. The next step is to choose those reflections which do agree in magnitudes and apply the signs of the calculated F values to the observed magnitudes. This yields a partial set of structure factors which may be substituted into the electron density series. The electron density function may then be calculated for all points in the unit cell. Even though the function may suffer from this series termination, it may well be that the peaks are sharp enough to indicate a shift in the atomic coordinates from the trial structure. Furthermore, and this is the greatest advantage, previously unspecified atom locations may show up while others are suppressed. A new structure is chosen from the electron density peaks and the structure factors re-calculated. If the trial structure has been close enough to the correct one, the new value of R is lower, with more of the structure factors being in agreement. From this new, more complete, set of structure factors the electron density function is again calculated; an iterative process.

This process is most effective in the initial stages of the structure determination, and only a very few iterations brought the value of R from .49 to .36. The electron density functions were created in the form of topographical maps via the computer programs of R. L. Hollis.

This procedure was unable to pinpoint the positions of the waters. Although the position of the $Na_2N_2O_2$ molecule was relatively unchanged throughout succeeding iterations, the water positions were more nebulous as the electron density peaks for these shifted from iteration to iteration.

The R Map

A procedure was devised to attack the problem of the shifty water molecules. Assuming that the coordinates representing the $Na_2N_2O_2$ molecule were essentially correct, these coordinates were fixed and the value of R calculated for this partial structure. A water molecule was placed at a given point in the unit cell and the value of R calculated for this new configuration. This was done for the water molecule in all positions in the unit cell. The position yielding the lowest R value was chosen as the proper position. Now this set of coordinates was fixed, another water molecule brought in and the procedure repeated.

Again, the method used was the topographical map technique with computations being performed on the computer. The results, unfortunately, were no more conclusive nor enlightening than those of the electron density map technique. The most satisfying results were obtained for 3 waters of hydration, and it was decided to proceed with refining techniques on the assumption that no atoms were greatly misplaced and the hope that the problem with the water positions would be explained by application of corrections for anisotropic thermal vibrations.

Taylor Expansion and Least Squares

Once the structure has been roughly established it remains only to make small shifts in the atom positions to yield the correct structure. Rather than make these shifts randomly, a procedure may be employed which guarantees that the changes are such as to lower the R value. This procedure is now derived.

Consider a function $g(x_1,x_2,\ldots x_n,y_1,y_2,\ldots y_n) \approx 0$. A small change in the x_i and y_i will make this approximation an equality. That is

$$g(x_1+\Delta x_1,\ x_2+\Delta x_2,\ldots y_n+\Delta y_n) = 0 \tag{26}$$

The problem is to find the Δx_i and Δy_i which will produce this result. To this end the function is expanded in a Taylor series, keeping only first order terms.

$$g(x_1+\Delta x_1,x_2+\Delta x_2,\ldots y_n+\Delta y_n) = g(x_i,y_i)+\Delta x_1\frac{\partial g}{\partial x_1}+\Delta x_2\frac{\partial g}{\partial x_2}+\ldots+\Delta y_n\frac{\partial g}{\partial y_n} \tag{27}$$

This equation is linear in the Δx_i and Δy_i. Given 2n such equations, the system may be solved for these quantities.

In this particular case

$$g(x_i,y_i) = F_c(hk\ell) - F_o(hk\ell) \tag{28}$$

There is one of these functions for every observed reflection, which yields more than the desired 2n equations, in general. To best fit such an overdetermined system, the method of least

squares is used. The sum of the functions $g_k(x_1+\Delta x_i, y_i+\Delta y_i)$ is required to be a minimum with respect to the variables Δx_i and Δy_i.

$$Y = \sum_k g_k^2$$

$$\frac{\partial Y}{\partial \Delta x_1} = \frac{\partial Y}{\partial \Delta x_2} = \ldots = \frac{\partial Y}{\partial \Delta y_n} = 0 \qquad (29)$$

This yields 2n equations in the 2n unknowns. More specifically,

$$\frac{\partial Y}{\partial \Delta x_1} = 2 \sum_k \left(\frac{\partial}{\partial x_1} g_k \Delta x_1 + \frac{\partial}{\partial x_2} g_k \Delta x_2 + \ldots + \frac{\partial}{\partial y_n} g_k \Delta y_n + g_k\right) \frac{\partial}{\partial x_1} g_k = 0$$

$$\frac{\partial Y}{\partial \Delta x_2} = 2 \sum_k \left(\frac{\partial}{\partial x_1} g_k \Delta x_1 + \frac{\partial}{\partial x_2} g_k \Delta x_2 + \ldots + \frac{\partial}{\partial y_n} g_k \Delta y_n + g_k\right) \frac{\partial}{\partial x_2} g_k = 0 \qquad (30)$$

$$\vdots$$

$$\frac{\partial Y}{\partial \Delta y_n} = 2 \sum_k \left(\frac{\partial}{\partial x_1} g_k \Delta x_1 + \frac{\partial}{\partial x_2} g_k \Delta x_2 + \ldots + \frac{\partial}{\partial y_n} g_k \Delta y_n + g_k\right) \frac{\partial}{\partial y_n} g_k = 0.$$

The system may be solved by the methods of matrix algebra and the coordinates changed accordingly. It has been assumed that these changes will be small, and if this is not the case the structure must be re-examined for major errors. Furthermore, the signs of the F_o values must be correct, since we are no longer dealing with magnitudes. Since the object of it all is to determine these signs, the problem appears to be circular. This is not the case, however. A partial set of structure factors may be used to initiate the procedure. If the majority of these signs are correct, the coordinate shifts will be of

sufficient accuracy to lower the R value. As the structure becomes more correct, more signs may be transferred from the calculated F values to the observed magnitudes and the coordinate shifts become more exact.

This is by nature an iterative process, even with a fixed number of F values, due to the Taylor Series' termination. The entire iterative procedure was programmed for the IBM 1410 (see Appendix I). For some reflections that were initially given the wrong sign, the refinement procedure indicated that these were indeed wrong by producing an F value much smaller in magnitude than that observed. This indicated that the number wanted to go through zero and back up the other way. Some F values fluctuated in sign, while others were very stable.

A typical run of the program had results as shown below. The base coordinates were taken from an electron density map.

Table 2. No. of reflections = 72.

Type	Base coordinates		Cycle No. 1		Cycle No. 2	
	X	Y	X	Y	X	Y
Na	.540	.030	.531	.025	.528	.027
O	.635	.100	.631	.115	.636	.110
O	.840	.143	.835	.141	.835	.141
O	.930	.280	.937	.199	.933	.202
O	.662	.243	.676	.244	.674	.242
O	.035	.025	.023	.021	.020	.020
Na	.059	.168	.054	.171	.050	.170
N	.280	.080	.287	.082	.286	.081
N	.372	.150	.374	.141	.366	.141
O	.632	.171	.523	.174	.519	.172
	R = .3838		R = .3473		R = .3312	

The most dramatic results occur in the first one or two cycles. After three or four cycles, the R value is changed only slightly and the data must be re-examined. More reflections may be added and/or signs may be changed on some of the F_o values in use. These new data are inserted with the latest set of co-ordinates as a base and the program run again. After several runs of the program, it is well to make a new electron density map. In this way, some atoms may be re-identified as to their type according to the size of the electron density peaks. Also, previously unspecified locations may appear on the map--a result not possible by use of the refinement program alone.

As may have been expected, the water molecules showed the greatest shifts, their positions fluctuating almost randomly and never actually settling into a stable configuration.

The advantage of this type of refinement is that the value of R is lowered directly as the differences between F_o and F_c are attacked. A disadvantage may crop up when the proper signs have not been chosen for all the F values in use. In such a case the coordinate shifts will be such as to lower R by adjusting the atomic coordinates improperly to accomplish this purpose.

Differential Synthesis

Similar in concept to the Taylor expansion on $F_c - F_o$, a procedure termed "differential synthesis" is often used in refinement. The two procedures are much the same, but here the function to be expanded is the first derivative of the electron

density function. This first derivative will be zero at an electron density peak, a local maximum. On the assumption that the coordinates of the unrefined structure are close to these peaks, a Taylor expansion is made, keeping only first order terms.

We have

$$g(x+\Delta x, y+\Delta y) = 0 = g + \Delta x \frac{\partial g}{\partial x} + \Delta y \frac{\partial g}{\partial y} \tag{31}$$

In this case

$$g(x,y) = \begin{cases} \frac{\partial \rho}{\partial x} \\ \frac{\partial \rho}{\partial y} \end{cases}$$

yielding two equations at the point (x,y),

$$\begin{aligned} \frac{\partial \rho}{\partial x} + \Delta x \frac{\partial^2 \rho}{\partial x^2} + \Delta y \frac{\partial^2 \rho}{\partial x \partial y} = 0 \\ \frac{\partial \rho}{\partial y} + \Delta y \frac{\partial^2 \rho}{\partial y^2} + \Delta x \frac{\partial^2 \rho}{\partial y \partial x} = 0 \end{aligned} \tag{32}$$

Such a pair of equations may be written for each atom and solved for Δx and Δy. Since

$$\rho(x,y) = \sum_h \sum_k F(hk0) \cos 2\pi(hx+ky) \tag{33}$$

(recall that the refinement is in the xy plane) the equations in matrix form reduce to

$$\begin{bmatrix} 2\pi\sum_{h,k} h^2C & 2\pi\sum_{h,k} hkC \\ 2\pi\sum_{h,k} khC & 2\pi\sum_{h,k} k^2C \end{bmatrix} \begin{bmatrix} \Delta x \\ \Delta y \end{bmatrix} = \begin{bmatrix} -\sum_{h,k} hS \\ -\sum_{h,k} kS \end{bmatrix} \qquad (34)$$

$$C=F(hk0)\cos 2\pi(hx+ky)$$

$$S=F(hk0)\sin 2\pi(hx+ky)$$

The advantage of this method is that it will not strain the lattice, as might the Taylor expansion on $F_c - F_o$. Each atom is treated individually, the corrections being made to place the atom on the nearby electron density peak. There is no guarantee that the R value will be lowered; if the closest peak to an atom is a wrong one, it will be placed there anyhow. The effectiveness of this procedure rests on the requirement that all atoms are initially located on the gradients of their respective electron density peaks. Enough of the F values must have the correct sign so that the proper electron density terrain is produced. If there are not enough F values, the functional terrain exhibits diffraction ripples, a series' termination effect. These ripples produce many local maxima and minima and may well cause the process to hang up. However, when this method is used and the R value is lowered from iteration to iteration, it is fairly certain that the structure is being correctly refined.

A computer program was written to utilize this technique, (See Appendix II), and used in conjunction with other refining procedures. Although it did not significantly lower the R value when in use, it did provide supporting results. When used in the region of R = .32, it did not significantly change atom

positions. This indicated that the lattice was not strained away from the electron density peaks, as might have been feared earlier.

RESULTS AND CONCLUSIONS

The atom locations as they now stand are as follows:

Atom	x	y
Na	.823	.068
Na	.057	.098
O	.651	.167
O	.245	.000
N	.542	.091
N	.357	.071
W	.350	.195
W	.248	.263
W	.090	.250

with an R value of .3179. An electron density map of the structure is shown in Plate VI. Many runs were made with the refinement programs, with all conceivable sign changes on the F_o values, until it became evident that this value of F was a lower limit for the type of structure proposed, with the data available. This is not to say that the model should be discarded. On the contrary, it is proposed that only minor changes need to be made; most probably, changes that involve locating (or relocating) a water molecule. The proposed structure exhibits a self-consistency and a symmetry which is appealing. Although anisotropic thermal vibration corrections could be applied and the R value certainly lowered further, it could not be done with a clear conscience. This process is usually begun in the vicinity of R = .20. It is assumed, however, that the water molecules will exhibit large thermal vibration amplitudes, in light of

EXPLANATION OF PLATE VI

Fig. 1. The electron density map for R = .34.

Fig. 2. The final model with R = .3179.

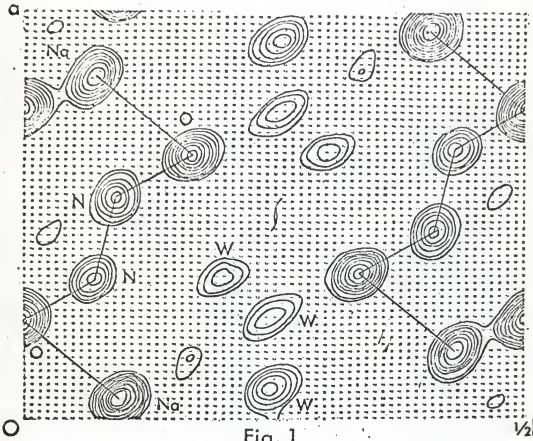


Fig. 1

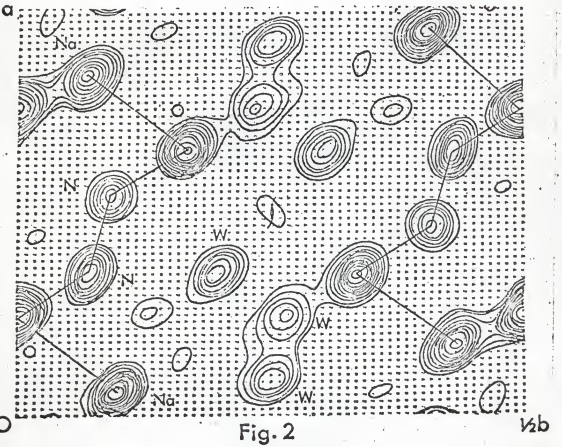


Fig. 2

present data.

The bond lengths, compared with values given in the International Tables for X-ray Crystallography, are as follows:

Type of bond	Observed	Expected
N-N	1.28 Å	1.23-1.40 Å
N-O	1.27 Å	1.22-1.45 Å
Na-O	2.42 Å	2.3-2.4 Å

From this it is to be inferred that the Na-O bond is nearly parallel to the xy plane. The O-N-N-O part of the molecule is assumed to be planar, so it is not unreasonable to hypothesize that the whole molecule is nearly parallel to the xy plane.

Further work in this area should be directed toward resolving the problem of loosely bound or free waters of hydration. After this, the z dimension of the crystal may be determined and anisotropic thermal vibration parameters taken into account. Before this is attempted, though, new crystals should be grown and an attempt made to gather more information for higher values of the ℓ Miller index, as the present lack of information on the c axis' rotation is inhibiting a complete solution.

APPENDIX I

The Least Squares Refinement Calculation

From earlier treatment it was seen that this type of operation on functions $g_k = 0$ yields matrix equations of the form

$$a_{ij} = \sum_k \frac{\partial g_k}{\partial x_i} \frac{\partial g_k}{\partial x_j}$$

$$b_i = - \sum_k g_k \frac{\partial g_k}{\partial x_i} \qquad \text{(I) - 1}$$

In this case

$$g_{\underline{h}} = 2 \sum_j f_j \cos 2\pi(hx_j+ky_j) - F_o(hk0) \qquad \text{(I) - 2}$$

and the matrix elements are

$$a_{ij} = \sum_{h,k} 16\pi^2 p f_i f_j \sin 2\pi(hx_i+ky_i) \cdot \sin 2\pi(hx_j+ky_j) \qquad \text{(I) - 3}$$

where $p = \begin{cases} h^2; & i \leq n,\ j \leq n \\ k^2; & i > n,\ j > n \\ hk; & i \leq n,\ j > n \quad \underline{\text{or}} \quad i > n,\ j \leq n \end{cases}$

and

$$b_i = \sum_{h,k} \left[F_c(hk0) - F_o(hk0)\right] 4\pi q f_i \sin 2\pi(hx_i+ky_i) \qquad \text{(I) - 4}$$

where $q = \begin{cases} h; & i \leq n \\ k; & i > n \end{cases}$

In practice, the matrix equation was set up and solved by elementary row operations. The coordinates were incremented accordingly and the process repeated. A cycle involving 22 coordinates and 60 reflections would take approximately ten minutes.

Provisions were made so that the number of reflections being used could be varied from the computer console while the program was running. Another feature controlled from the console was one by which the sign of F_o could be changed if F_c indicated that this was desirable. As the value of R was calculated, during each cycle, it was printed on the console typewriter. Thus, the operator could decide when the process should be terminated and more data added or changes made.

The program could handle a variable number of unique atoms, up to 11, and up to 100 reflections. There is provision made for three atom types. This much is completely general, applying to the two-dimensional refinement of any centrosymmetric structure whose variables fall within the above bounds.

Advantage was taken of the symmetry relations of space group $P2_1/b$, so that the equations in the program are not completely general. To adapt the program to another (centrosymmetric) space group, the equations contained in the DO loop on statement number 102 must be changed accordingly. This is the portion of the program which calculates equation (28).

The listing of the program (Plate VII) does not read easily; the approach is expedient towards speed and minimum memory requirements.

Output consisted of the cycle number, the coordinates, calculated and observed F values, and R.

EXPLANATION OF PLATE VII

The next four pages show the FORTRAN program for least squares refinement.

PLATE VII

```
      MON$$      JOB        TAYLOR FIT
C  DATA IS LOADED AS FOLLOWS
C (1)CARD CONTAINING NUMBER OF ATOMS AND NUMBER OF REFLECTIONS,
C     PER FORMAT 1
C (2)DECK OF COORDINATES AND ATOM TYPES, FORMAT 2
C (3)DECK OF H, K, ATOMIC SCATTERING FACTORS (3 ATOM TYPES),
C       AND OBSERVED F VALUES, FORMAT 3
C
      REAL K1
      DIMENSION$(100),X(11),Y(11),NT(11),ASF(100,3),H(100),
     1 K1(100),FO(100),A(22,22),C(100),D(100)
    1 FORMAT(2I4)
    2 FORMAT(F5.3,2X,F5.3,2X,7X,I2)
    3 FORMAT(2F3.0,3(4X,F6.4),14X,E9.3)
    5 FORMAT(12X,F6.3,2X,F6.3,7X,I2)
    8 FORMAT(1HL,9X,20HITERATED COORDINATES/14X,1HX,7X,1HY,8X,
     1 4HTYPE/)
    9 FORMAT(1H1,10X,12HCYCLE NUMBER,I3,1H,,2X,I3,
     1 12HREFLECTIONS)
   10 FORMAT(1HL,19X,2HR=,F6.4)
   11 FORMAT(1HL,3X,1HH,3X,1HK,3X,1HL,9X,10HOBSERVED F,5X,
     1 12HCALCULATED F/)
   12 FORMAT(1X,2I4,3X,1HO,9X,F7.2,9X,F7.2)
 1025 FORMAT(1HL,18HMATRIX IS SINGULAR)
      REWIND4
      REWIND5
      REWIND6
      IC=1
      JC=0
C****LOAD DATA
      READ(1,1)NOA,NOB
      N=2*NOA
      READ(1,2)(X(I),Y(I),NT(I),I=1,NOA)
      DO99I=1,NOB
   99 READ(1,3)H(I),K1(I),(ASF(I,L),L=1,3),FO(I)
C****BEGIN ITERATION LOOP,CREATE A AND B MATRICES BY COLUMNS
      DO93MOP=1,21
      RN=0.
      RD=0.
      DO50I=1,NOB
   50 B(I)=0.
      CALL CONSOL(NOB,IC,JC)
      MP=MOP-1
      WRITE(3,9)MP,NOB
      WRITE(3,8)
      DO101I=1,NOA
  101 WRITE(3,5)X(I),Y(I),NT(I)
```

```
      WRITE(3,11)
      DO102J=1,NOA
      M=NT(J)
      T1=6.28318530717958468*X(J)
      T2=6.28318530717958468*Y(J)
      DO100I=1,NOB
      ARG1=T1*H(I)+T2*K1(I)
      B(I)=B(I)+4.*ASF(I,M)*COS(ARG1)
  100 C(I)=25.132741228718338872*ASF(I,M)*SIN(ARG1)
      WRITE(5)(C(I),I=1,NOB)
  102 WRITE(6)(C(I),I=1,NOB)
      REWIND5
      REWIND6
      DO118J=1,NOA
      READ(5)(D(I),I=1,NOB)
  118 WRITE(4)(D(I),I=1,NOB)
      REWIND4
      REWIND5
      DO103I=1,NOB
      J=H(I)
      K=K1(I)
C----WRITE CALCULATED AND OBSERVED F VALUES
  150 IF(IC.EQ.0)GOTO151
      F=B(I)*FO(I)
      IF(F.LT.0.)FO(I)=-FO(I)
  151 IF(JC.EQ.0)GOTO152
      F=(B(I)-FO(I))/(B(I)+FO(I))
      IF(F.LE.-.30)FO(I)=-FO(I)
  152 WRITE(3,12)J,K,FO(I),B(I)
      F=ABS(B(I))-ABS(FO(I))
      B(I)=B(I)-FO(I)
C-----CALCULATE RESIDUAL R AND WRITE
      RN=RN+ABS(F)
  103 RD=RD+ABS(FO(I))
      R=RN/RD
      NR=R*100000.
      CALL POINT (NR)
      WRITE(3,10)R
C****STOP HERE WHEN NUMBER OF ITERATIONS IS SATISFIED
      IF(MOP.EQ.2)GOTO200
C****CREATE LEAST SQUARES SYSTEM FOR A AND B
      L=4
      M=5
      DO112I=1,NOA
      IP=I+NOA
      READ(6)(C(K),K=1,NOB)
      DO111J=1,I
```

```
      JP=J+NOA
      A(IP,JP)=0.
      A(IP,J)=0.
      A(I,J)=0.
      READ(M)(D(K),K=1,NOB)
      DO 110 K=1,NOB
      F=C(K)*D(K)
      A(IP,JP)=A(IP,JP)+F*K1(K)*K1(K)
      A(IP,J)=A(IP,J)+F*K1(K)*H(K)
  110 A(I,J)=A(I,J)+F*H(K)*H(K)
      A(JP,IP)=A(IP,JP)
      A(J,IP)=A(IP,J)
  111 A(J,I)=A(I,J)
      REWINDM
      K=L
      L=M
      M=K
  112 CONTINUE
      REWIND6
      DO1131=1,NOB
      D(I)=B(I)
  113 B(I)=0.
      DO1141=1,NOA
      IP=I+NOA
      READ(5)(C(J),J=1,NOB)
      DO114K=1,NOB
      F=C(K)*D(K)
      B(I)=B(I)+F*H(K)
      B(IP)=B(IP)+F*K1(K)
  114 CONTINUE
      REWIND5
C****SOLVE MATRIX SYSTEM FOR THE DELTA X AND DELTA Y VALUES
      DO1003KK=2,N
      K=KK-1
C*****TEST FOR ZERO DIAGONAL, INTERCHANGE ROWS.
      IF(A(K,K).NE.0.)GOTO1006
      DO1005I=KK,N
      IF(A(I,K).EQ.0.)GOTO1005
      F=B(K)
      B(K)=B(I)
      B(I)=F
      DO1007J=K,N
      F=A(K,J)
      A(K,J)=A(I,J)
 1007 A(I,J)=F
      GOTO1006
 1005 CONTINUE
```

```
      WRITE(3,1025)
      STOP
C*****REDUCE A TO UPPER TRIANGULAR
 1006 DO1001J=KK,N
 1001 A(K,J)=A(K,J)/A(K,K)
      B(K)=B(K)/A(K,K)
      A(K,K)=1.
      DO1003I=KK,N
      F=A(I,K)
      DO1002J=K,N
 1002 A(I,J)=A(I,J)-F*A(K,J)
 1003 B(I)=B(I)-F*B(K)
      IF(A(N,N).EQ.0.)WRITE(3,1025)
      IF(A(N,N).EQ.0.)STOP
      F=A(N,N)
      A(N,N)=1.
      B(N)=B(N)/F
C*****REDUCE A TO IDENTITY
      DO1010KK=2,N
      I=KK-1
      DO1010K=KK,N
      F=A(I,K)
      B(I)=B(I)-F*B(K)
      DO1010J=K,N
 1010 A(I,J)=A(I,J)-F*A(K,J)
C****INCREMENT THE COORDINATES WITH THE DELTA X AND Y VALUES
C*****AND WRITE
      DO93I=1,NOA
      X(I)=X(I)+B(I)
      J=I+NOA
   93 Y(I)=Y(I)+B(J)
C****RECYCLE ON ITERATION LOOP
  200 STOP
      END
```

APPENDIX II

The Differential Synthesis Calculation

The explicit equations for this calculation have already been given. This is a much less complicated procedure than the least squares approach, although not as effective in lowering the R value. The program is completely general, applicable to any centrosymmetric space group, with one exception. The equation in which $F_c(hk\ell)$ is calculated has been simplified by taking advantage of the symmetry relations. $F_c(hk\ell)$ has the FORTRAN name, FC(I), in the program, and the calculation is contained in the DO loop on statement number 98.

The program accepts up to 11 unique atoms of three different types, and up to 72 reflections. Machine capacity was no real problem, so that the number of reflections could be extended to 100 by changing the DIMENSION card. Each coordinate correction involves solving a 2x2 matrix equation. A cycle could be completed in 5 minutes for 22 coordinates and 60 reflections. Output consisted of coordinates, the x and y values, calculated and observed F values, the R value, and the root mean square correction. A printout of this program is shown in Plate VIII.

EXPLANATION OF PLATE VIII

The next two pages show the FORTRAN program for the differential synthesis refinement.

PLATE VIII

```
MON$$     JOB  DIFF SYNTH
   DIMENSION AH(72),AK(72),ASF(72,3),FO(72),FC(72),X(11),Y(11),
  1  NT(11),A(2,2),B(2)
 1 FORMAT(2I4)
 2 FORMAT(F5.3,2X,F5.3,9X,I2)
 3 FORMAT(2F3.0,3(4X,F6.4),14X,E9.3)
 4 FORMAT(1H1,10X,22HDIFFERENTIAL SYNTHESIS,10X,14,12H REFLECTI
  1ONS, 10X,5HCYCLE,I3//20X,11HCOORDINATES,10X,11HCORRECTIONS//
  2  14X,4HTYPE,4X,1HX,6X,1HY,12X,2HDX,5X,2HDY)
 5 FORMAT(15X,I2,2X,F5.3,2X,F5.3,9X,F5.3,2X,F5.3)
 6 FORMAT(/35X,6HSIGMA=,F6.4)
 7 FORMAT(1HL,12X,1HH,3X,1HK,3X,1HL,3X,5HOBS F,10X,6HCALC F/)
 8 FORMAT(10X,2I4,3X,1HO,1X,F7.2,9X,F7.2)
 9 FORMAT(/25X,2HR=,F6.4)
   READ(1,1)NOA,NOB
   READ(1,2)(X(I),Y(I),NT(I),I=1,NOA)
   DO15I=1,NOB
15 READ(1,3)AH(I),AK(I),(ASF(I,M),M=1,3),FO(I)
   DO200NCYCLE=1,3
   RN=0.
   RD=0.
   S=0.
   DO16I=1,NOB
16 FC(I)=0.
   K=NCYCLE-1
   WRITE(3,4)NOB,K
   DO100J=1,NOA
   B(1)=0.
   B(2)=0.
   A(1,1)=0.
   A(1,2)=0.
   A(2,1)=0.
   A(2,2)=0.
   T1=6.2831853071*X(J)
   T2=6.2831853071*Y(J)
   M=NT(J)
   DO98I=1,NOB
   ARG=T1*AH(I)+T2*AK(I)
   FC(I)=FC(I)+4.*ASF(I,M)*COS(ARG)
   AT=FO(I)*COS(ARG)
   BT=-FO(I)*SIN(ARG)
   A(1,1)=A(1,1)+AH(I)*AH(I)*AT
   A(1,2)=A(1,2)+AH(I)*AK(I)*AT
   A(2,2)=A(2,2)+AK(I)*AK(I)*AT
   A(2,1)=A(1,2)
   B(1)=B(1)+AH(I)*BT
98 B(2)=B(2)+AK(I)*BT
```

```
      DO97I=1,2
      DO97K=1,2
   97 A(I,K)=6.2831853071*A(I,K)
      CALL SOLN(A,B,2)
      WRITE(3,5)M,X(J),Y(J),B(1),B(2)
      S=S+(B(1)*B(1)+B(2)*B(2))
      X(J)=X(J)+B(1)
  100 Y(J)=Y(J)+B(2)
      S=SQRT(S/(FLOAT(NOA)*2.))
      WRITE(3,6)S
      WRITE(3,7)
      DO19I=1,NOB
      J=AH(I)
      K=AK(I)
   19 WRITE(3,8)J,K,FO(I),FC(I)
      DO21I=1,NOB
      RN=RN+ABS(ABS(FO(I))-ABS(FC(I)))
   21 RD=RD+ABS(FO(I))
      R=RN/RD
      NR=R*100000.
      CALL POINT(NR)
      NS=S*100000.
      CALL SIGMA(NS)
  200 WRITE(3,9)R
      STOP
      END
```

ACKNOWLEDGMENT

The author wishes to express his sincere thanks to Dr. R. D. Dragsdorf for his guidance and motivation throughout this project. Appreciation is also in order for Mr. Ralph Hollis, a research partner, for his valuable contributions and his inspiring dedication. The staff members of the computing center are to be thanked for their patience and cooperation. The project was sponsored by the United States Air Force Office of Scientific Research.

BIBLIOGRAPHY

Buerger, M. J.
Crystal Structure Analysis. John Wiley (1962).

Chang, Shih Chi.
The Investigation of the Crystal Structures of Sodium Hyponitrite and Potassium Nitrite. Ph.D. Dissertation, Kansas State University (1963).

Cullity, B. D.
Elements of X-Ray Diffraction. Addison-Wesley (1959).

Dragsdorf, R. Dean, Shih Chi Chang, and Ralph L. Hollis.
"The Crystallography of Solid Nitrogen Oxides." Report, U. S. Air Force, AF-AFOSR-61-24. Kansas State University (1964).

Hauptmann, H., and J. Karle.
Solution of the Phase Problem I. The Centrosymmetric Crystal. A. C. A. Monograph No. 3, Brooklyn: Polycrystal Book Service (1953).

McLachlan, D.
X-Ray Crystal Structure. McGraw Hill (1957).

Patterson, A. L.
Z. Krist. 90: 517-42 (1935).

Sax, M., P. Bearskens, and S. Chu.
The Crystal Structure of - Nitroperoxybenzoic Acid.
Acta Crystallographica, 18: 252 (1965).

Stucky, G., J. Lambert, and R. D. Dragsdorf.
The Hydrates of Sodium Hyponitrite. To be published.(1966).

Woolfson, M. M.
Direct Methods in Crystallography. Oxford University Press (1961).

A FURTHER INVESTIGATION OF THE CRYSTAL STRUCTURE OF SODIUM HYPONITRITE

by

GLEN PATRICK REESE

B. S., Montana State College, 1963

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Physics

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1967

Previous study of sodium hyponitrite has indicated a trans structure in the $N_2O_2^{--}$ ion. The unit cell parameters and space group have been determined and a list of structure factor magnitudes prepared. The cell is monoclinic with the space group $P2_1/b$. The cell parameters are

$$a = 7.22 \pm .03 \text{ Å}$$
$$b = 17.10 \pm .07 \text{ Å}$$
$$c = 6.01 \pm .02 \text{ Å}$$
$$\gamma = 107.5 \pm .4^\circ$$

The statistical methods of Karle and Hauptmann were used in an attempt to determine signs for the structure factors, but failed due to lack of sufficient data for the ℓ Miller index.

The Patterson function was computed for the structure and indicated a high degree of symmetry. A trial structure was selected from the Patterson section at $w = \frac{1}{2}$ and treated with alternate electron density maps and structure factor calculations. The number of waters of hydration and their positions were not well-defined, but refinement was attempted. Refinement techniques included the least squares method and differential synthesis. Both of these were programmed for the IBM 1410.

The structure indicated has a present R value of .3179 and coordinates as follows:

Atom Type	x	y
Na	.823	.068
Na	.057	.098
O	.615	.167
O	.245	.000
N	.542	.091
N	.357	.071
W	.350	.195
W	.248	.263
W	.090	.250

This structure must remain tentative until further data are gathered on the l Miller indices and the problem of the water positions is resolved. Extensions to be indicated involve the solution for the z dimension and refinement techniques involving thermal vibration parameters.